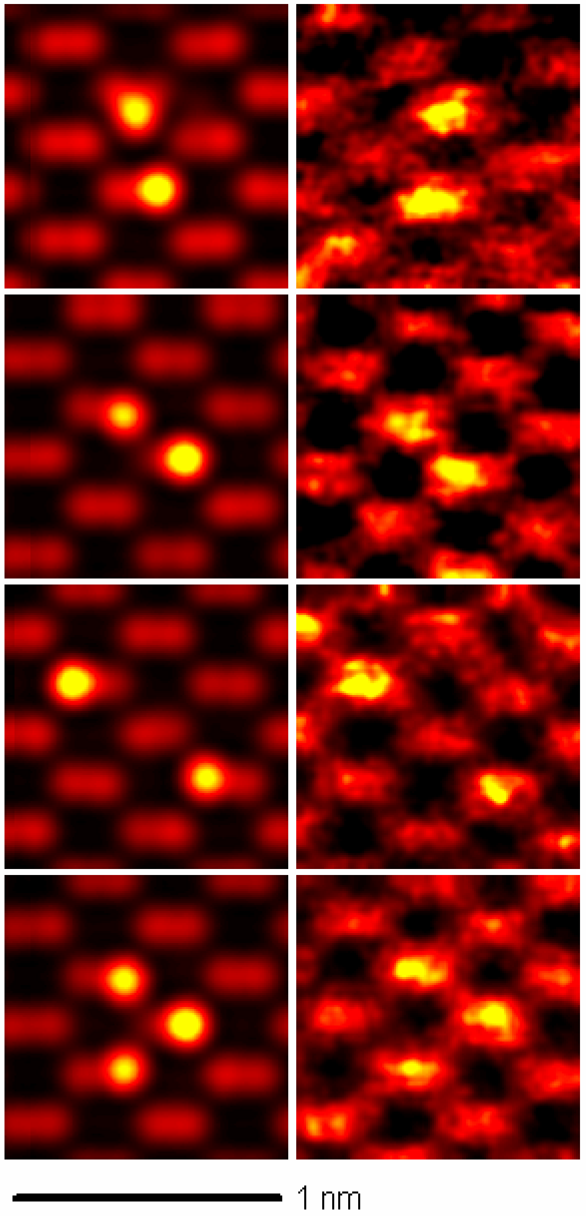


# Future Nanocharacterization with Electrons: sub-Ångstrom, sub-eV, and Single Atom

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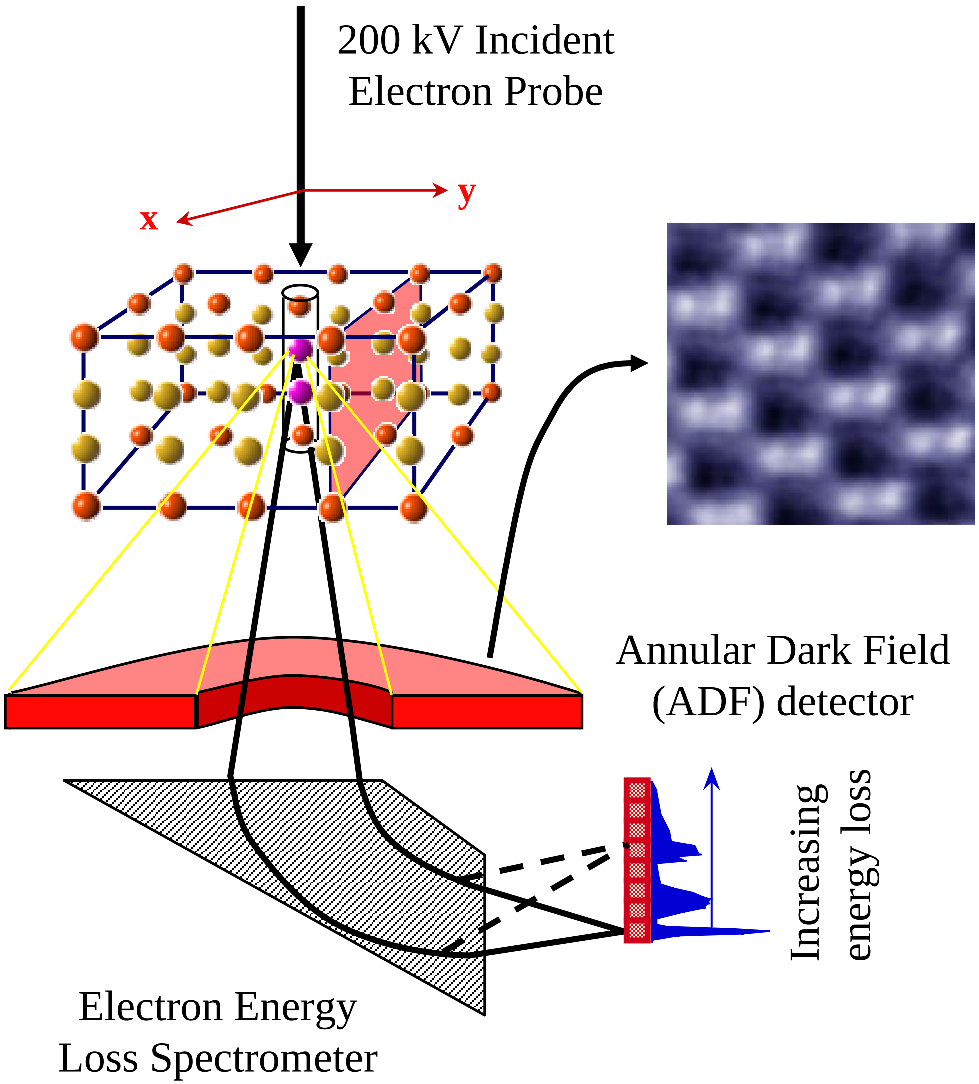
# Overview

- New technology and new capabilities: aberration correctors and monochromators
- New applications:
  - imaging and chemical analysis with single-atom sensitivity
  - imaging & spectroscopy of point defects
  - local valence-band spectroscopy
  - 3D, atomic scale imaging by tomography and optical sectioning
  - coherent scattering at nanometer resolution

# Scanning Transmission Electron Microscope



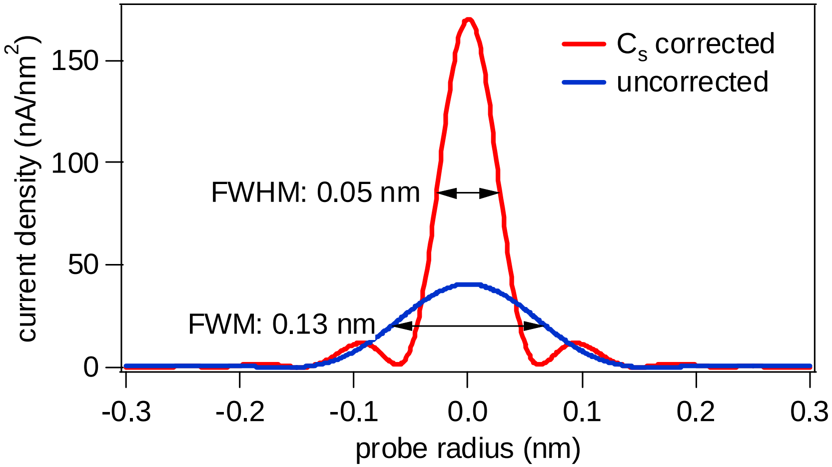

- atomic diameter probe raster scanned
- high-angle detector (no Bragg beams)
- low-angle, BF, and spectrometer also available
- views structure in projection along the beam direction

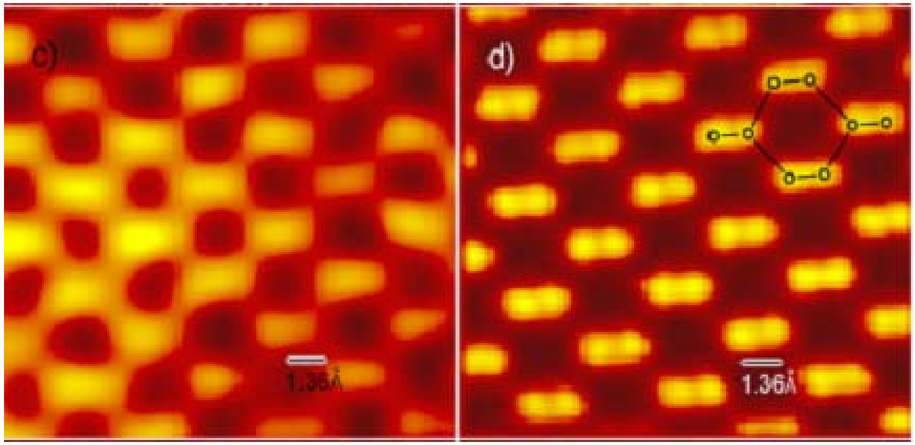
# Aberrations & Correcting Them

Current electron lenses have large 3rd order spherical aberration:

optical micrograph


same micrograph with EM-like $C_s$



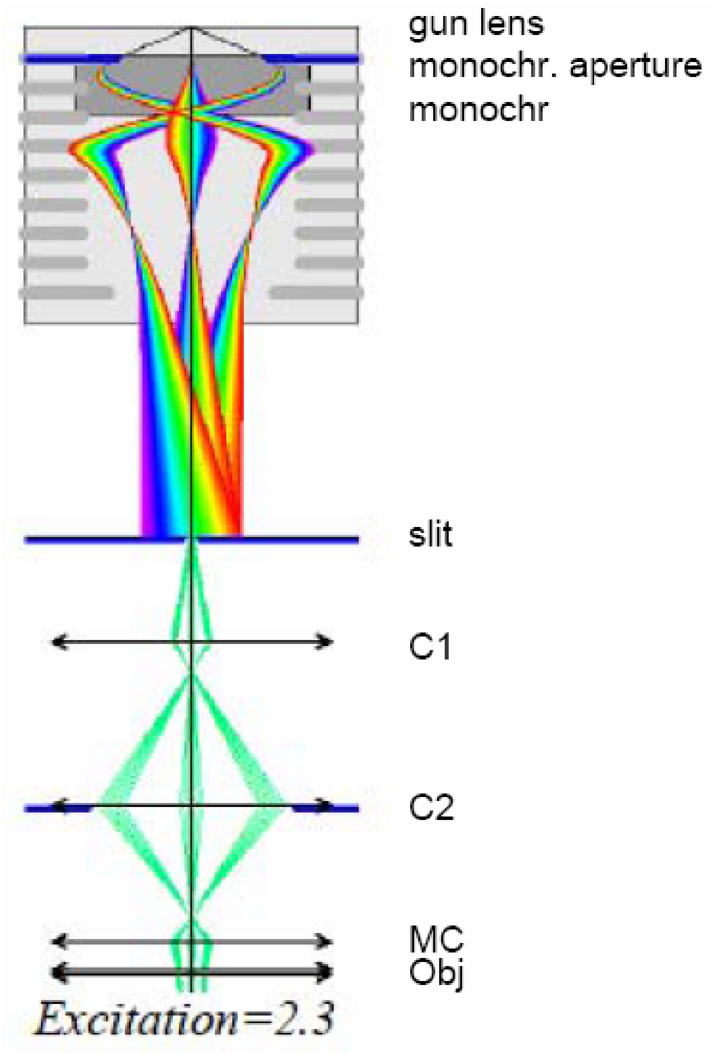

P.E. Batson, N. Dellby, O.L. Krivanek, Nature **418**, 617 (2002).



Optical micrographs from www-cyanosite.bio.purdue.edu/ images/images.html

# Monochromators

- TEM spectroscopic resolution limited by ΔE of the beam.
- Beam ΔE controlled by e-e scattering near the emitter.
- Cold field-emitter can achieve 0.3 eV; more common Schottky emitter 0.7 eV.
- Monochromator uses a slit in an energy dispersion plane to reduce ΔE.
- 0.15 eV achievable on Schottky system, 0.06 eV on a cold FEG.



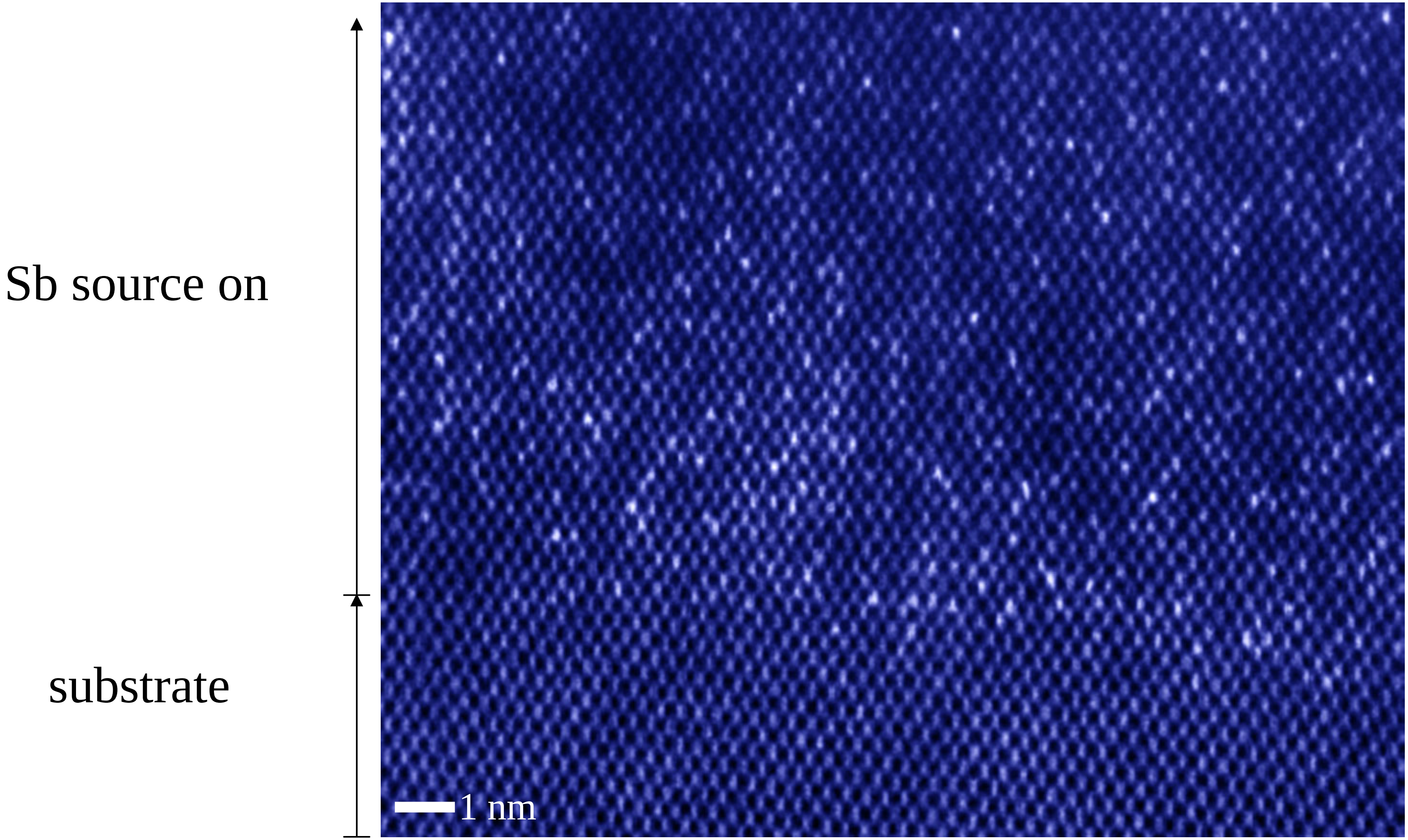

P.C. Tiemeijer, *Inst. Phys. Conf. Ser.* **161,** 191 (1999).

P.E. Batson, H. W. Mook, P. Kruit, *Inst. Phys. Conf. Ser.* **165,** 213 (2000)

# DoE TEAM Project

- TEAM = Transmission Electron Achromatic Microscope
- Build the world's first chromatic aberration corrected TEM.
- First instrument for NCEM @ LBL concentrated on highest achievable resolution.
- Subsequent instruments planned for other DoE e-beam centers @ UIUC, ORNL, and ANL.
- $C_s$ and $C_c$ correction could allow 1 Å resolution with a sample area of ~1 cm, allowing much more flexibility in *in situ* experiments.

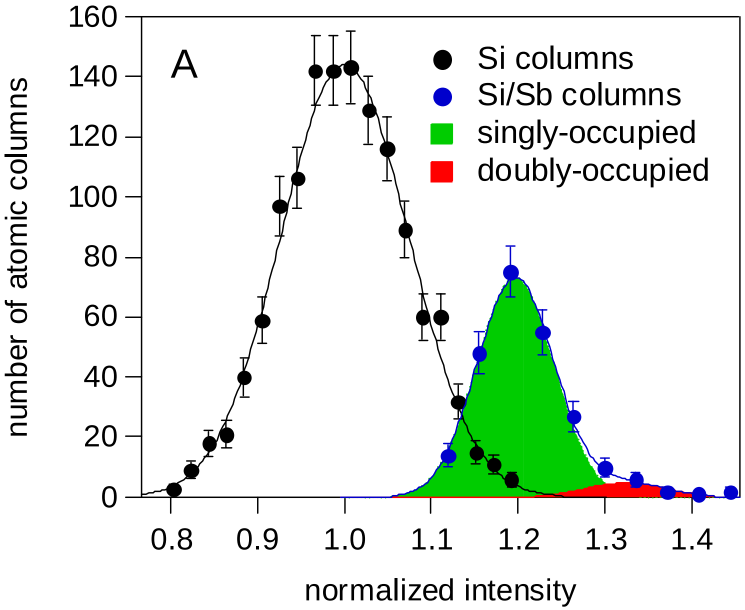
# Imaging Single Atoms




Most of the brightest dots are atomic columns with one Sb.

# Imaging Single Atoms

| | Image A | | Image B | |
|---|---|---|---|---|
| # of Sb atoms | measured | predicted | measured | predicted |
| 0 | 1300 (50) | 1300 | 2240 (70) | 2234 |
| 1 | 230 (30) | 223 | 470 (40) | 468 |
| 2 | 15 (15) | 17 | 20 (20) | 45 |

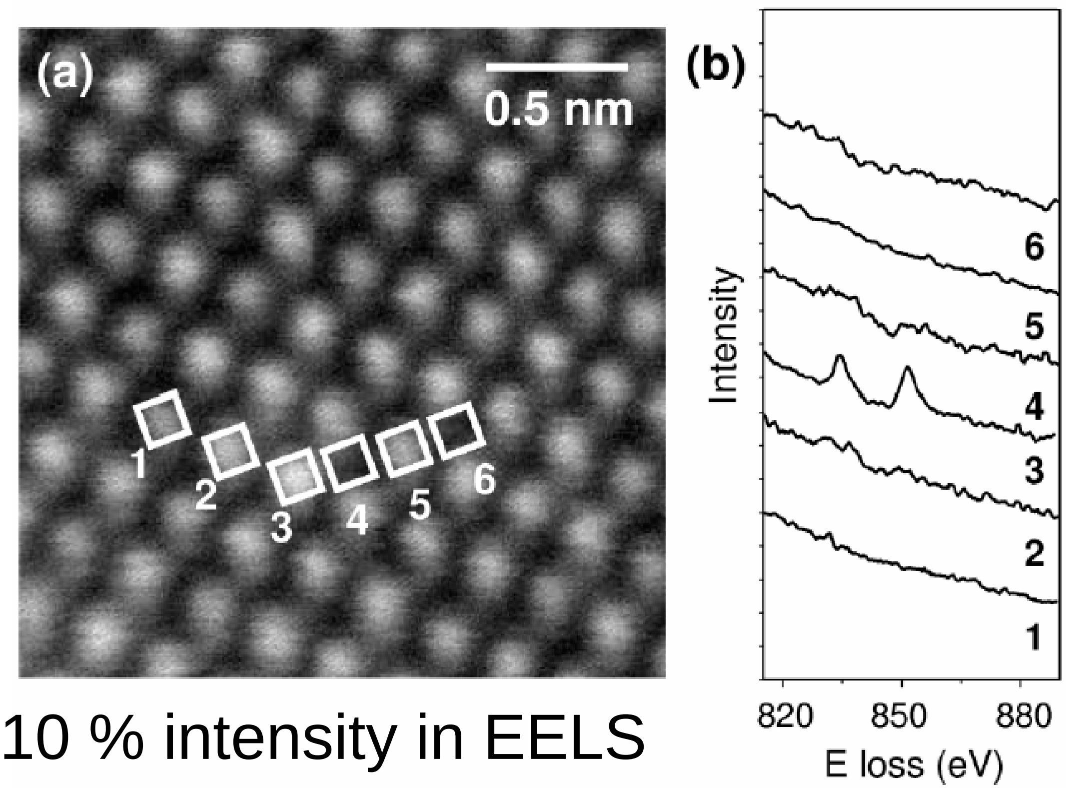



Results are consistent with random substitution of Sb on Si sites, measured with single-Sb sensitivity and ~100 % Sb detection efficiency.

First time single atoms have been imaged *in the bulk!*.

P. M. Voyles, D. A. Muller, J. Grazul, P. H. Citrin, and H.-J. Gossmann, Nature **416**, 826 (2002).

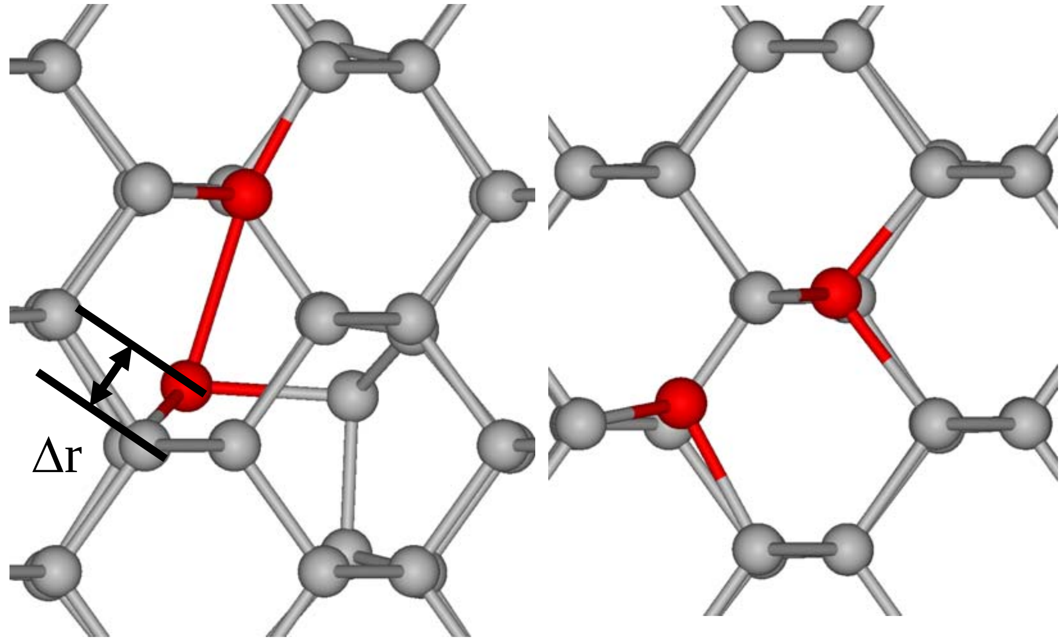
# Chemistry of Single Atoms



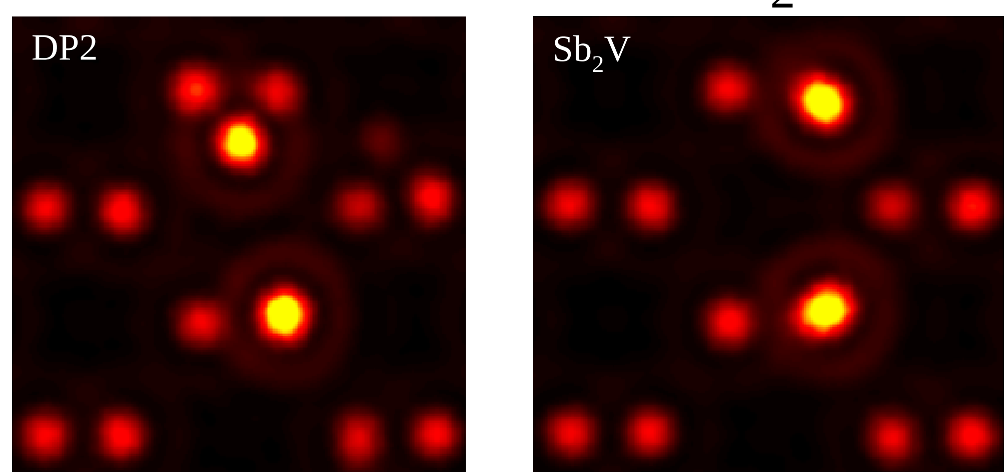

- Varela et al. Phys. Rev. Lett. **92**, 095502
- Aberration corrected STEM.
- Sample is lightly La doped $CaTiO_3$
- Column 3 contains one La atom; spectrum 3 shows La $M_{4,5}$ edge
- Column 2 is Ti, shows ~10 % intensity in EELS
- Column 4 is O, shows ~20 % intensity in EELS
- Points the way to single-atom electronic structure
  - valence of isolated impurities
  - natural or artificial charge ordering
  - trap states in semiconductors

# Point Defect Complexes in Si

- At high concentration, donor impurities stop donating in Si.
- Various donor / point defect clusters proposed.
- Can’t see the point defects directly, but with a aberration corrected STEM could see the off-site displacement of the heavy donor atoms.

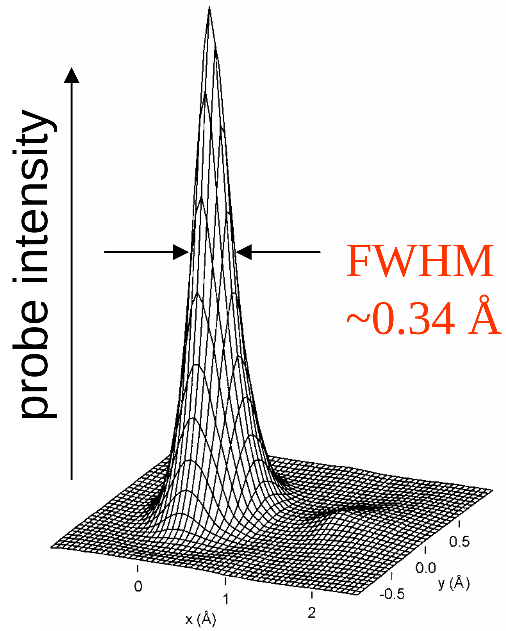


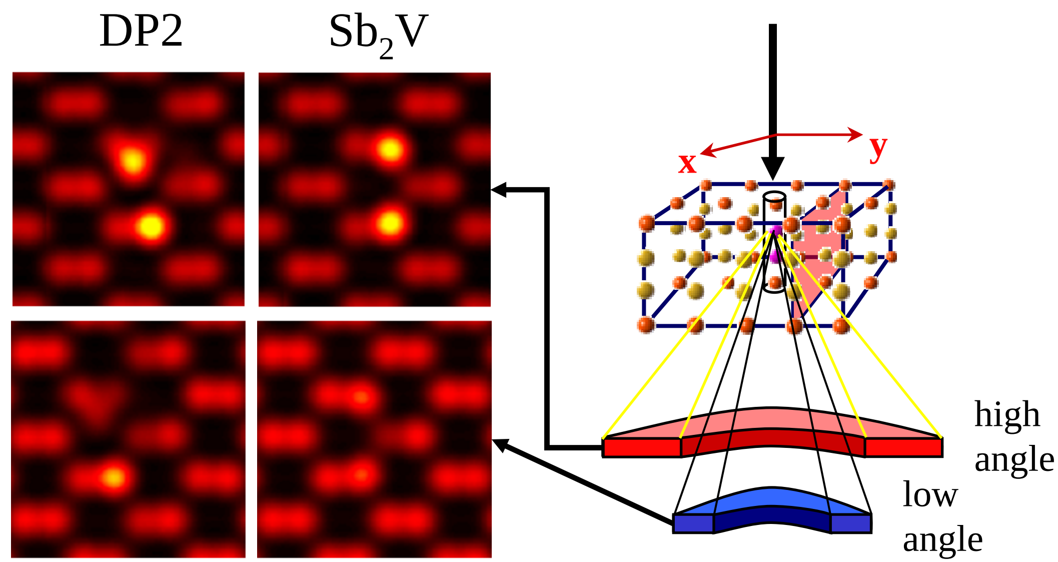

DP2 $\quad$ $Sb_2V$




Simulated aberration-corrected STEM images

# Probe Channeling

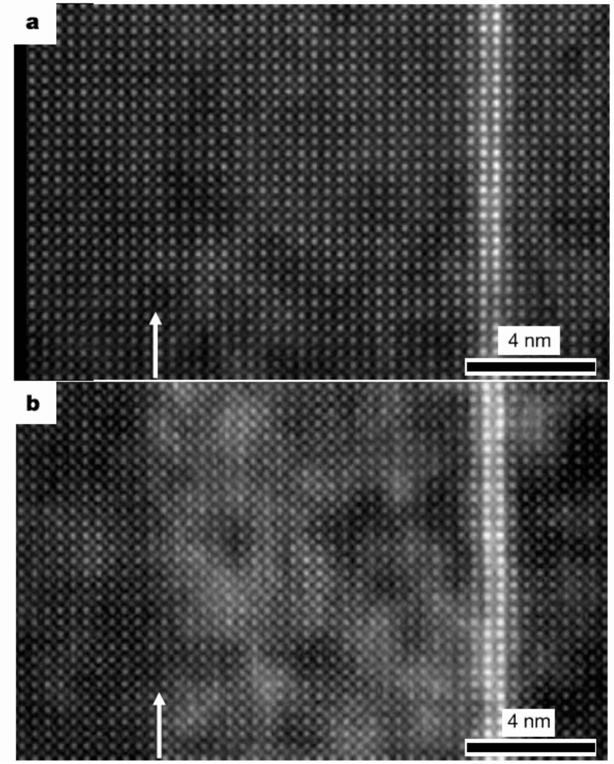


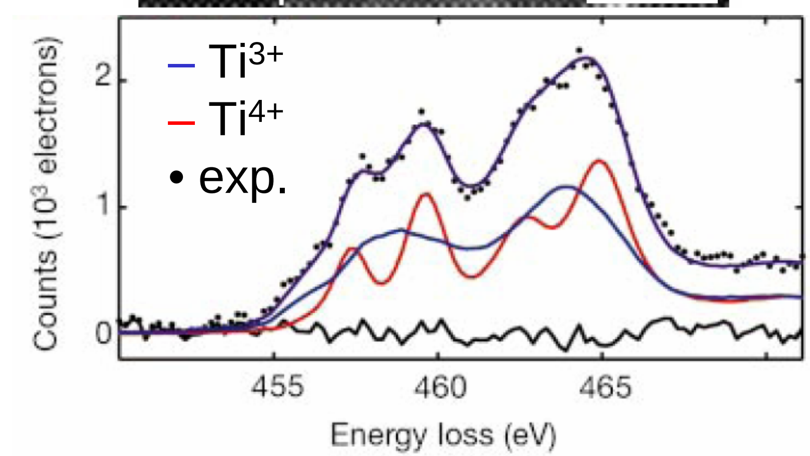




- Probe $e^-$ couple to 1*s* state localized on the atomic column, acting like a local resolution boost for on-site impurities.
- Compare high-angle image emphasizing heavy atoms, to low-angle image emphasizing the lattice: Sb with large $\Delta r$ will disappear.
- Result is that all Sb's have $\Delta r < 0.3$ Å, requiring a new model for the electrically deactivating defect.
- Voyles et al. PRL **91**, 125505 (2003).

# O Vacancies in $SrTiO_3$

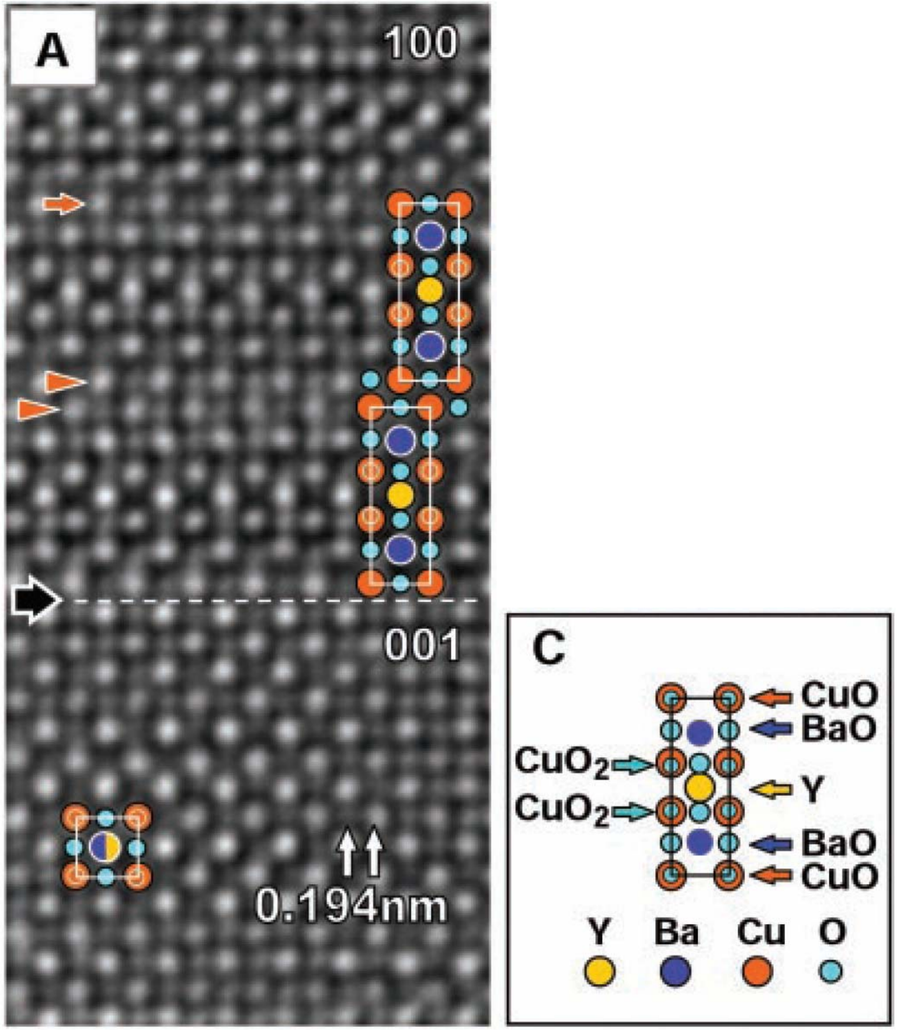
- Muller et al., Nature **430,** 657 (2004).
- PLD homoepitaxial $SrTiO_{3-\delta}$; $\delta$ varied by O partial pressure
- Vacancies appear in
  - O K-edge fine structure directly
  - Ti $L_{2,3}$ edge, which is sensitive to Ti valence
  - LAADF image via strain-induced dechanneling
- Detection limit 1-4 $O_V$



# Imaging Anions Directly

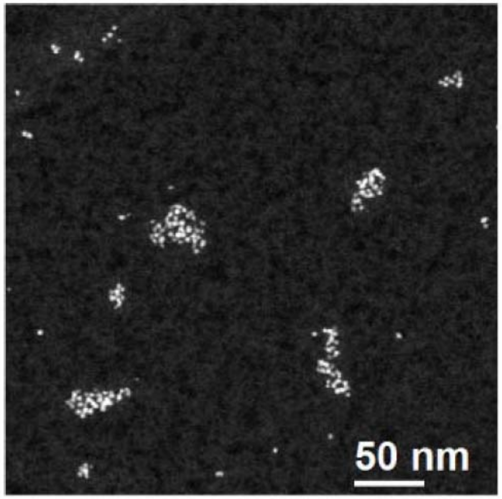
- Jia et al. Science **299,** 871 (2003).
- $C_s$ corrected TEM gives phase contrast, which is more sensitive to light atoms.
- O columns between Cu/O columns are resolved.
- Recent reports of detecting O vacancies by quantifying contrast, but have not been demonstrated on well-controlled samples.

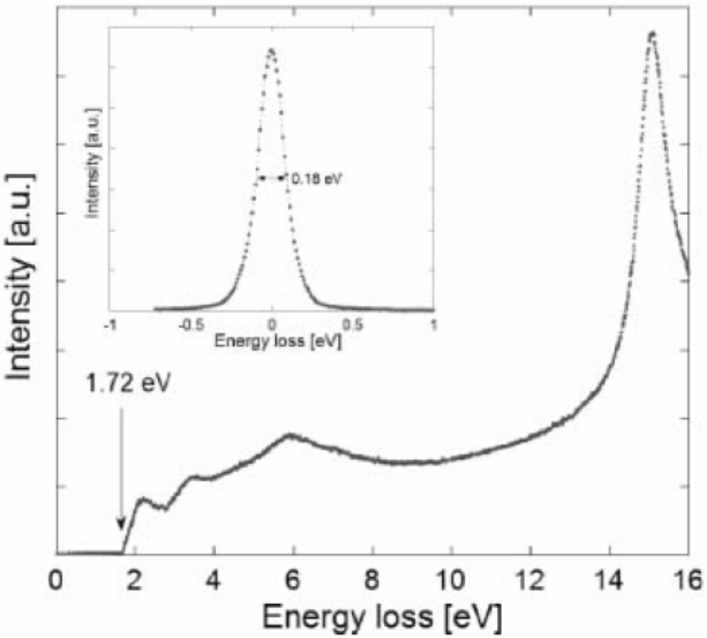



90° tilt boundary in $YBa_2Cu_3O_7$

# Interband Scattering by EELS

- High ΔE from monochromator makes transition to conduction band visible in low-loss EELS.
- Measurements on single nanostructures:
  - Correlate bandgap, surface states, etc. with size, shape, atomic structure, and surface chemistry.
  - Measure anisotropy in single quantum dots.
  - R. Ermi, N. D. Browning, Microsc. Microanal. **10 Suppl. 2,** 842 (2004).
- Band bending at e.g. interfaces, edges of quantum wells.

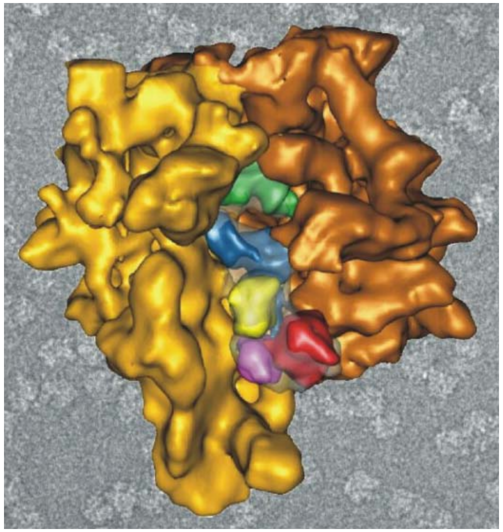


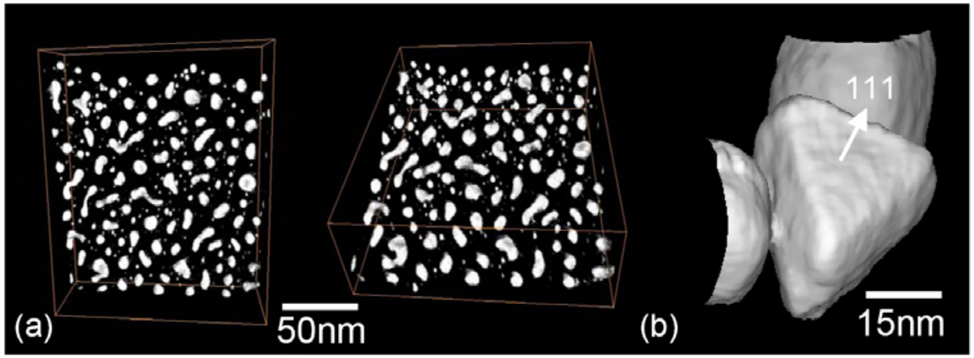



# 3D: Tomography

- Requires monotonic intensity response with thickness.
- Commonplace in biology, where diffraction effects are minimal.
- Z-contrast STEM & energy-filtered TEM are enabling materials applications.
- 1 nm resolution achievable in 3D.
- EFTEM adds chemical information.

J. Harms et al., Structure Fold Des 7, 931-41. (1999)

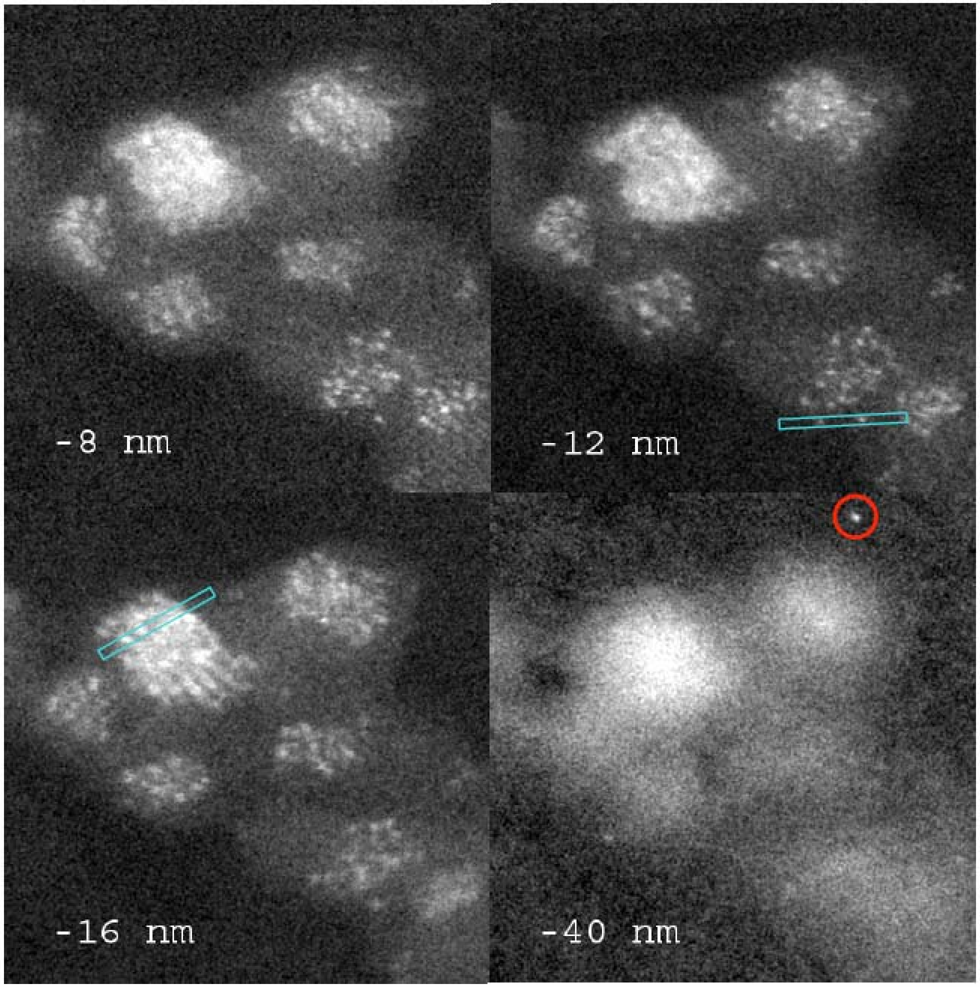





P. A. Midgley et al., Microsc. Microanal. **10 Suppl. 3**, 148 (2004).

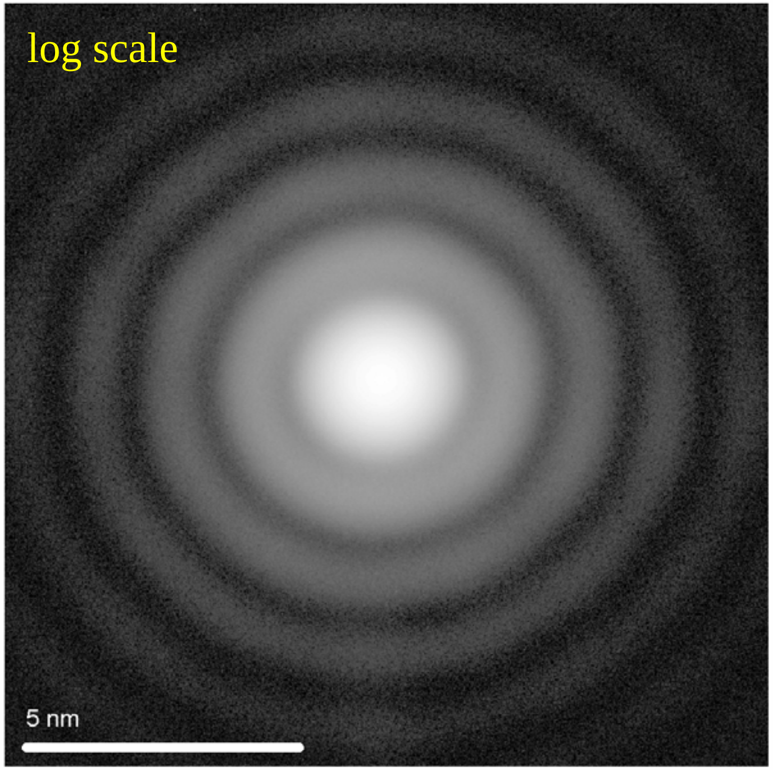
# 3D: Optical Sectioning

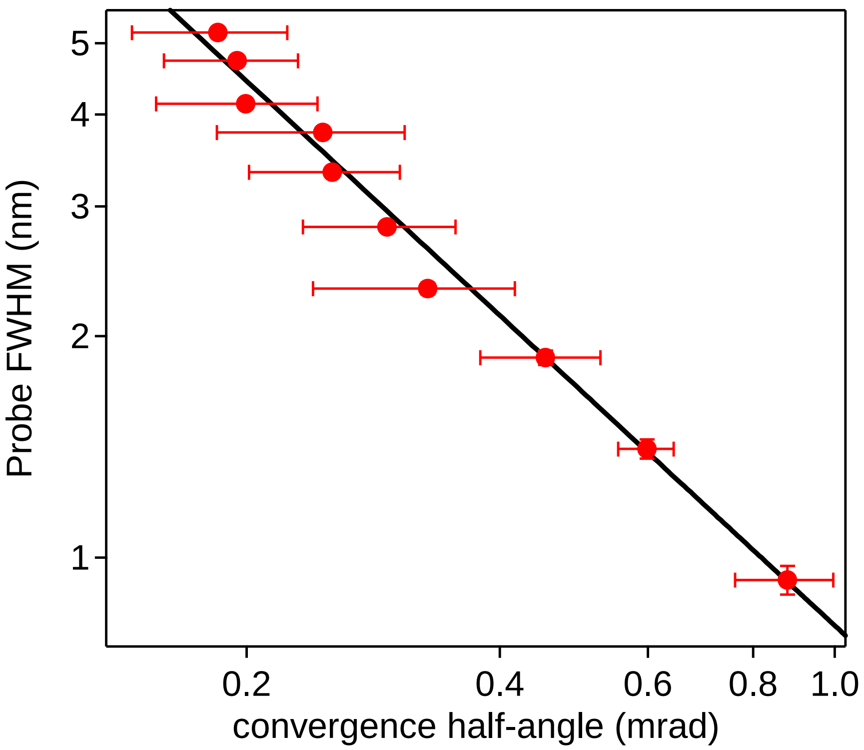
- Aberration correction means larger numerical apertures, limited depth of field.
- 3D imaging by a defocus series; optical sectioning.
- Current instruments vertical resolution of 6 nm
- Next generation 1.5 nm.




Through focus series of $Pt_2Ru_4$ catalyst on a-C support. Pennycook et al. Microsc. Microanal. **10 Suppl. 3**, 1172 (2004).

# Coherent Scattering

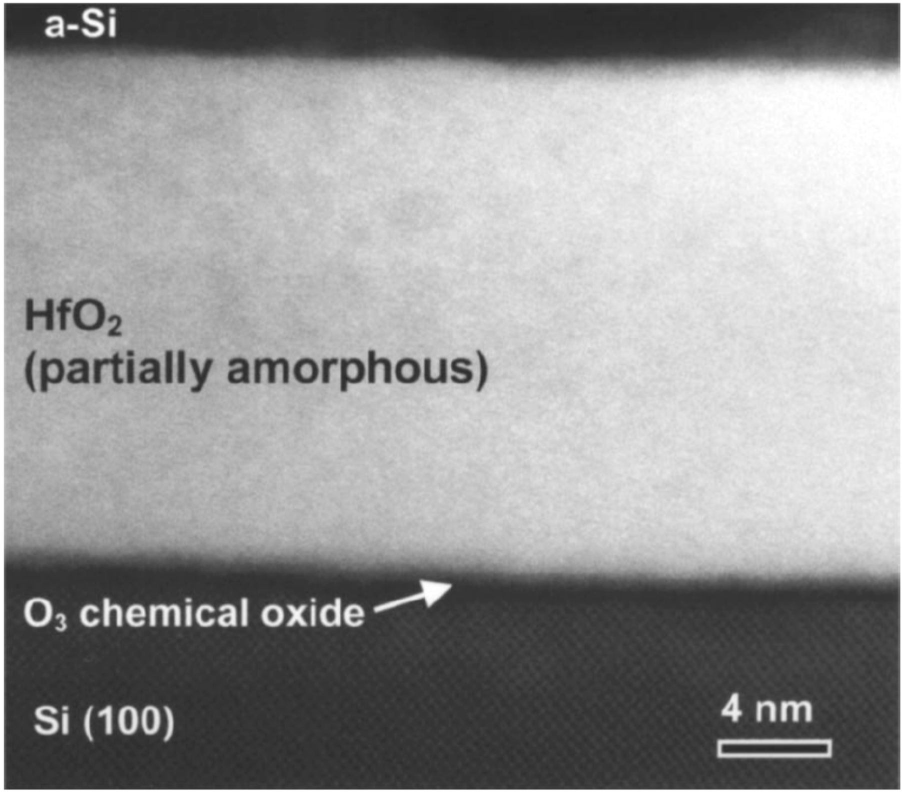



- High brightness field-emission sources can create coherent electron probes 0.5 – 5 nm in diameter.

# Amorphous Thin Films

- Pair distribution function is the basic structural diagnostic for amorphous materials.
- McBride [Ultramic. **76**, 115 (1999)] developed a method for measuring PDF from ~2 nm volumes by deconvolution of convergent probe.
- Useful for thin films, interface layers, integrannular layers.

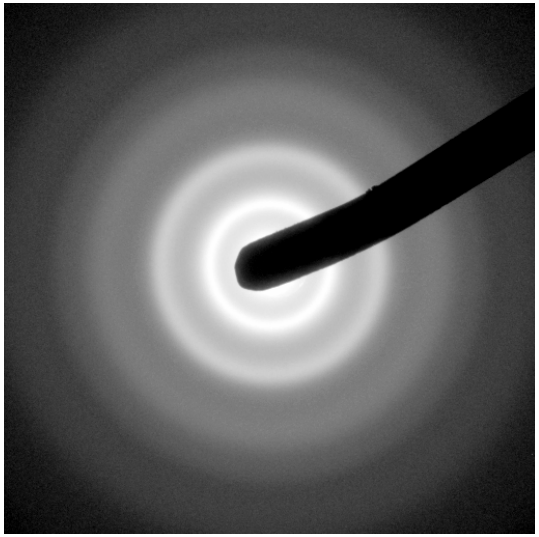



$HfO_2$ replacement gate dielectric with “amorphous” but heavily ordered structure (Ho et al. JAP **93**, 1477 (2003).

# Spatial Fluctuations in Diffraction

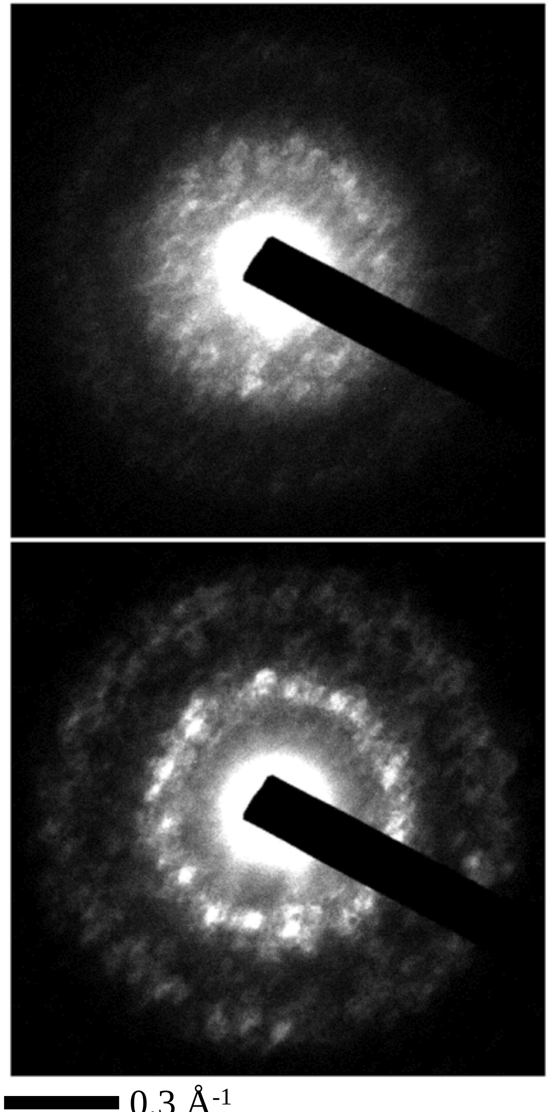
- Coherent probe size ≅ structural correlation length.
- Magnitude of spatial fluctuations reveals heterogeneities in amorphous structure.
- Spatial analogy to photon correlation spectroscopy.

Large area: average $S(q)$



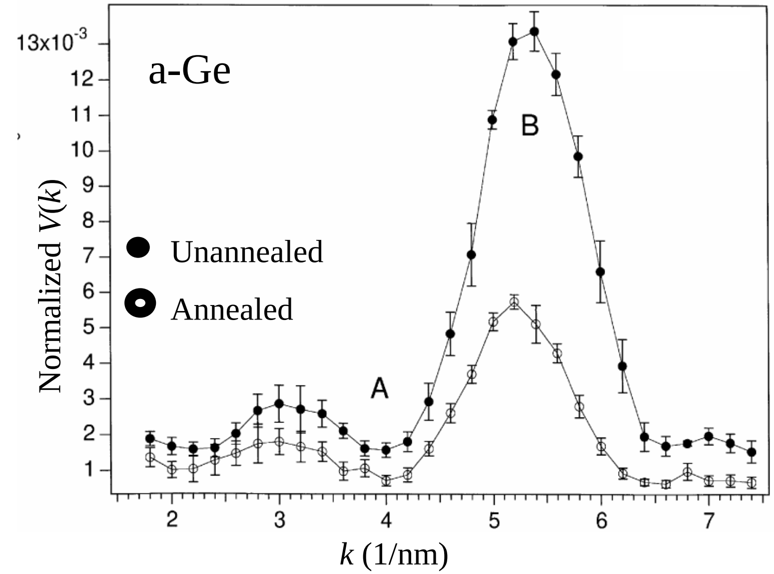
Voyles and Muller, Ultramicroscopy **93**, 147 (2002).

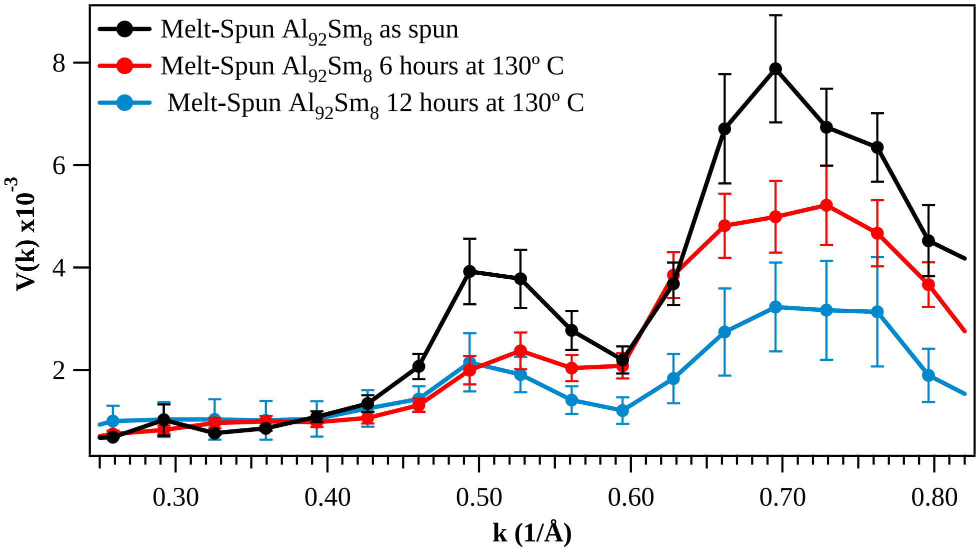
Different 1.5 nm areas:



# Fluctuation TEM

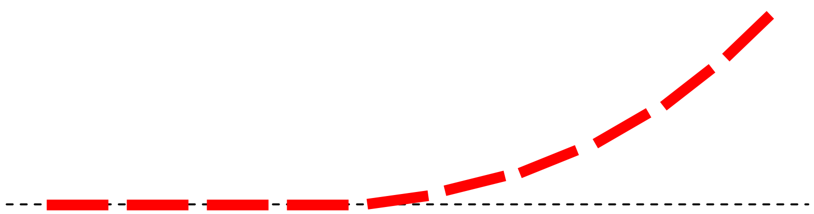
- Real amorphous semiconductors are not ideal continuous random networks (Gibson and Treacy PRL **78**, 1074 (1997).
- Al-Sm metallic glass with high critical cooling rate contains structural order (Stratton et al. MRS Proc. **806** M9.4 (2003).

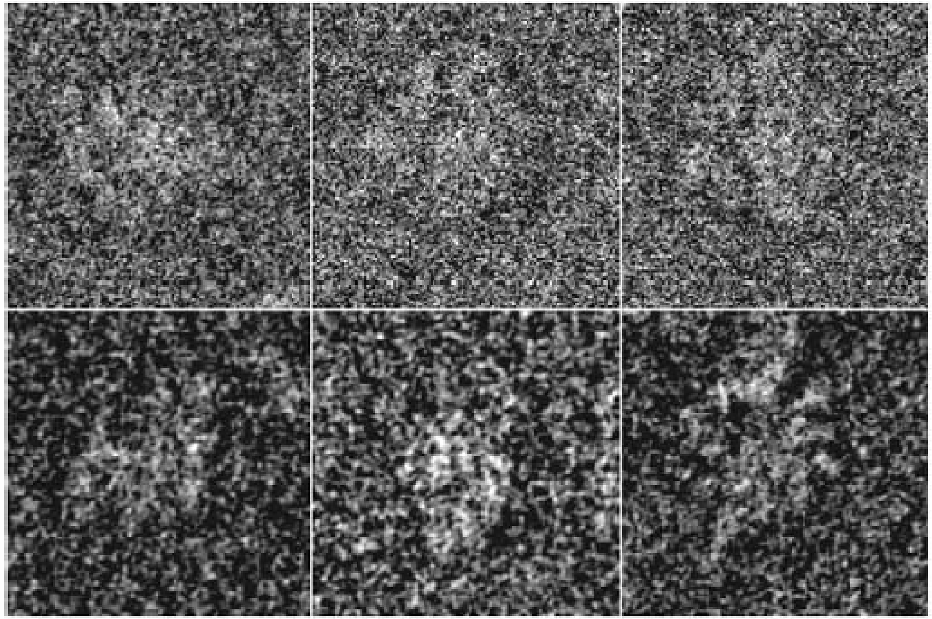


# Future Applications: Biomaterials

- Persistence length in polymers from angular correlation along the chain.
- Phase separation in block copolymers
- Proteins
  - single particles in amorphous ice
  - set of many single-particle patterns contain more data than the average





70*S* ribsomes from *e. coli* imaged in different orientations (Gao et al. Ultramicroscopy **93**, 169 (2002)

# Perennial Limitations

- Samples must be thin
  - <10 nm for high-resolution measurements on typical crystals
- Samples must be in vacuum
  - Some environmental cell work in gas (Lee et al. Rev. Sci. Inst. **62**, 1438 (1991)) and now liquid environments (Williamson et al. Nature Materials **2**, 532 (2003)).
- Radiation damage
  - Several applications (e.g. spectroscopic identification of oxygen vacancies) limited by signal to noise, which is fundamentally limited by damage.
  - 3D imaging will require very high dose.

# Summary

- Current or near-future EM offers:
  - Structural and chemical characterization at sub-Ångstrom resolution and single atom sensitivity.
  - Characterization of point defects under the right conditions.
  - <0.2 eV resolution spectroscopy of individual nanostructures, impurities, & defects.
  - 3D, nanometer resolution imaging
  - Nanoscale coherent scattering for characterization of amorphous materials